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Zero-discharge Technology for Production of Nanocrystalline Cellulose

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ABSTRACT

In this paper a green zero-discharge technology for production of nanocrystalline cellulose particles (NCP) was proposed. The parameters of acid hydrolysis of bleached kraft pulp were studied. As a result the following optimal conditions were found: concentration of sulphuric acid is 60 wt. %, liquid/solid ratio is 5, temperature is 45°C and time is 1 h. Cellulose hydrolysis under optimal conditions generates NCP with average sizes of 120 x 15 nm, yield of 60-64%, crystallinity degree of 73-75%, DP of 120-140 and content of sulfonic groups of 46-50 meq/kg. The proposed technology provides the complete utilization of acidic wastewater and their use for the production of valuable by-product such as superphosphate fertilizer, the selling of which covers above 70% of the production cost of NCP. Furthermore, all washing water is returned in the production line. Thus, the cheap cellulose nano-product, 40% wetcake of NCP, was obtained without discharge of production waste into the environment. The obtained wetcake of NCP can be used as modifying additive for compositions of papers, glues, coatings, latexes or solutions of polymers, followed by homogenization, casting and drying.

Keywords: *Nanocrystalline cellulose; Green technology; Waste utilization; By-product*

INTRODUCTION

Being natural nanostructured polymer cellulose consists of nano-scale fibrils built of ordered nanocrystallites and low ordered non-crystalline (amorphous) nanodomains statistically alternated along the fibril [1]. The nanocrystallites having three-dimensional order are strong and inaccessible structural elements. As against, the low-ordered non-crystalline domains having twisted and curved segments are weak and accessible places of the fibrils. Thereby, cleavage of glycosidic bonds at the hydrolysis occurs mainly in non-crystalline domains of cellulose nanofibrils that facilitates release of rod-shape nanocrystalline particles (NCP).

The history of NCP began 65 years ago, when Rànby reported for the first time that colloidal suspensions of cellulose can be obtained by controlled sulfuric acid-catalyzed degradation of cellulose fibers [2]. Practically, NCP are prepared by hydrolysis of cellulose samples with enough concentrated solutions of sulfuric acid at moderate temperatures combined with following mechanical or ultrasound treatment. Currently, NCP are obtained from celluloses of various origins: cotton, wood pulp, ramie, hemp, flax, sisal, microcrystalline cellulose and some other sources.

The concentration of sulfuric acid (SA) can vary from 50 to 70 wt. % and the hydrolysis time can be from several minutes at temperature of 60-70°C to overnight at low temperature, 25-30°C [3-6]. Typical hydrolysis conditions are: concentration of SA is 63-65 wt. %, temperature 40-50°C and time 1-2 h [7, 8]. The nanocrystalline particles prepared from various celluloses with typical yield of 20-30% have width from 4 to 50 nm and length from 50 to 500 nm.

Nanocrystalline particles of cellulose are characterized by increased crystallinity, developed specific surface, biodegradability, stability to aggressive medium, increased temperatures and proteolytic enzymes, etc. [9]. Due to these features, NCP particles have diverse potential application as reinforcing additive for papermaking, high-quality filler for polymer composites, glues and coatings, nano-carrier of biologically and therapeutically active substances, etc. [10-12].

Despite abundant investigations, the existing lab methods for isolation of cellulose nanocrystalline particles are far from the optimal. Firstly, these methods are complex, multi-stage and low productive. Secondly, the production methods of NCP are based on the use of expensive feedstock and requires a high consumption of chemicals, water and energy. Thirdly, the existing production methods are accompanied by formation of huge volumes of acidic wastewater polluting the environment. As a result, the production cost of NCP is extremely high. Therefore it is not surprising that nanocrystalline particles of cellulose are not profitable to produce on an industrial scale.

The main purpose of this paper was to develop an improved cost-save technology for production of nanocrystalline cellulose particles without polluting the environment.

MATERIALS AND METHODS

Materials

Bleached Kraft pulp of Weyerhaeuser (USA) having 92% α-cellulose and DP =1100 was chosen as an initial feedstock. Besides, the technical grade 95% sulfuric acid, sodium carbonate and hydroxylapatite were used.

Methods

The degree of crystallinity of the cellulose samples was determined by method of wide angle X-ray scattering, WAXS [13]. Size and shape of the nanoparticles were investigated by method of field emission gun scanning electron microscopy (EM) [14]. Concentration of sulfonic groups in the nanoparticles was calculated from a sulfur assay [15]. The average degree of polymerization, DP, was measured by the viscosity method using diluted solutions of cellulose in Cadoxen [16].

RESULTS AND DISCUSSION

Typical lab method for preparation of NCP was described in [7]. Sample of microcrystalline cellulose (MCC) was mixed with deionized water for swelling to accelerate the impregnation process of the sample by concentrated sulfuric acid (SA) having a high viscosity. The MCC-suspension in water was put in an ice bath and stirred while concentrated SA was added by drop until the desired liquid to solid ratio (LSR) of about 10 and acid concentration of about 64 wt. % was reached. The acidic treatment was carried out at 45^{o}C for 2 h while stirred. Then cellulose sediment was separated from the acid solution and washed by centrifugation. The centrifuge step was stopped after five washing cycles at least. The product was dialyzed with deionized water until the wash water maintained at neutral pH. To break up aggregates and isolate individual NCP, the washed product was diluted with water to 1% concentration and sonicated for 30 min.

Analysis of the lab method showed the following drawbacks, which hinder its use for industrial technology of NCP. Firstly, MCC is very expensive feedstock worth $10-15 per kg. Secondly, both dialysis and sonication techniques are not suitable for industrial production. Thirdly, the consumption of chemicals, water and energy is very high. Fourthly, the use of 63-65 wt. % SA leads to low yield of NCP. Fifthly, huge volumes of wastewater remain not recycled and pollute the environment. Sixthly, dilute dispersion of NCP is not appropriate as an industrial product. Finally, due to the mentioned drawbacks the production cost of NCP is extremely high.

As a consequence, it is necessary to develop an improved technology that will be suitable for industrial production of NCP. This technology is based on the idea to recycle the acidic wastewater and its use as feedstock to produce a valuable by-product, the selling of which can cover part of production expenses of nano-product. Another idea is that the production of the NCP will be carried out directly at a pulp mill using the produced pulp for a low cost as a feedstock. The scheme of the production process of the cellulose nano-product and by-product was shown in Figure1.

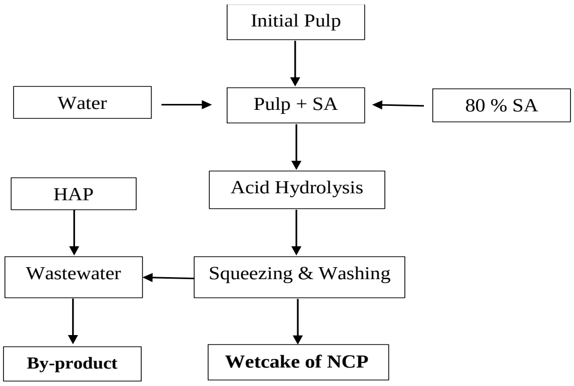

Figure1. *General scheme of production process.*

Small-pilot experiments were performed to find the optimal conditions of production process. The used feedstock was bleached Kraft pulp, which can be supplied by the pulp mill at a reduced cost of about $0.35 per kg. One kilo of this pulp was cut into pieces of 1-3 cm in size. The pulp pieces were mixed with water in

Waring-blender, and the resulting slurry was squeezed up to final solids content of 40-50 wt. %. The wet pulp was put into 10-L glass reactor placed in cooled water bath, and then 80 wt. % sulfuric acid was slowly added while stirring to obtain the required final concentration of SA (50 to 65 wt. %) and LRS of about 5. The reactor was heated in a water bath to 45°C and maintained at this temperature for 0.5-2 h while stirring to hydrolyze the cellulose. After acidic treatment the bath is cooled to room temperature, and double volume of water was added into reactor while stirring to stop the hydrolysis process. The sediment of hydrolyzed cellulose was separated from the acid solution by centrifugation at acceleration of 5000 *g* for 10 min, and additionally washed three times separating the acidic water by centrifugation.

The washed sediment containing low amount of residual acid was complete neutralized with 10% sodium carbonate, twice washed and centrifuged to obtain cellulose nano-product, i.e. wetcake containing of about 40% of NCP, whereas all acidic wastewater was collected together and neutralized with powdered hydroxylapatite (HAP) to obtain the superphosphate as a by-product, as follows:

$$7H_2SO_4 + 2Ca_5(PO_4)_3OH \rightarrow \underline{3Ca(H_2PO_4)_2\ x\ 7CaSO_4} + 2H_2O$$

Neutral wastewater is returned to the production line to use for wetting of pulp, preparation of solutions and washing of hydrolyzed cellulose.

The results showed that the yield of NCP does not change until the acid concentration does not exceed 60 wt. % (Fig. 2).

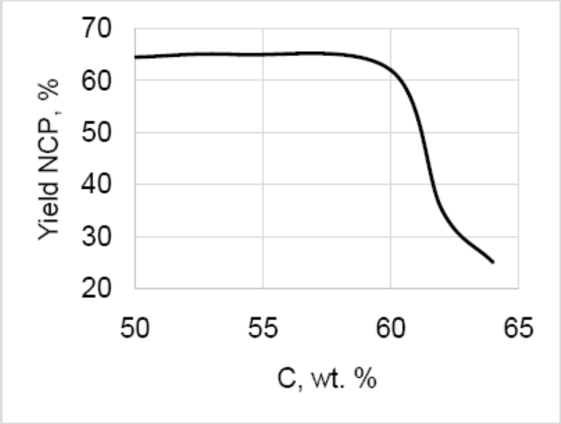

Figure2. *Dependence of yield of NCP on acid concentration in hydrolysis stage*

From EM studies it follows that hydrolysis with 50 wt. % acid gives relatively large particles, but after cellulose hydrolysis with 60-64 wt. % acids the sizes of NCP can be decreased (Figures 3, 4).

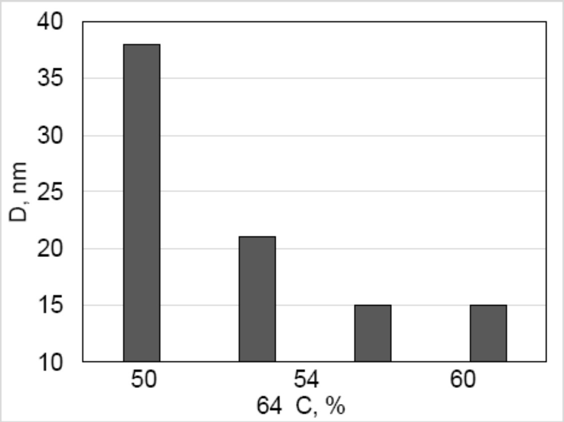

Figure3. *Dependence of average diameter of NCP on acid concentration in hydrolysis stage*

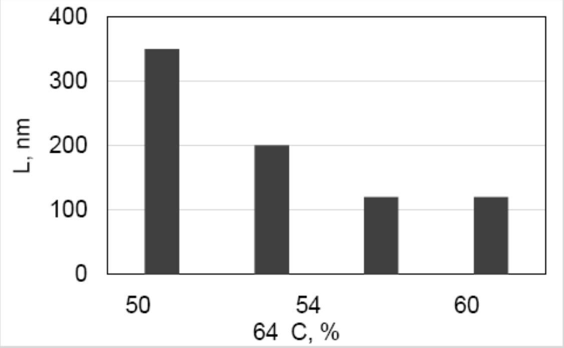

Figure4. *Dependence of average length of NCP on acid concentration in hydrolysis stage*

As a result of the research, the following optimal hydrolysis conditions of bleached Kraft pulp were found: concentration of SA is 60 wt. %, LSR is 5, temperature is 45°C, time is 1h, which provide the production of nanocellulose with yield of 62%. The nanocrystalline particles of cellulose with average size of 120 x 15 nm have crystallinity degree of 73-75%, DP of 120-140 and content of sulfonic groups of 46-50 meq/kg (Table1).

Table1. *Characteristics of nanocrystalline cellulose particles*

Characteristics	Value
Average sizes of NCP, nm	120 x 15 nm
Type of crystalline allomorph	CIβ
Degree of crystallinity, %	73-75
Degree of polymerization	120-140
Content of SO3H-groups, meq/kg	46-50

The obtained wetcake of NCP can be used as modifying additive for compositions of paper, glues, coatings, latexes or solutions of polymers, followed by homogenization, casting and drying to obtain materials with improved properties.

The final task of this study was to evaluate the production cost of primary product – wetcake of NCP, using e.g. 1 t of the pulp. To implement the economic calculations the following parameters were taken into account: price of initial pulp, cost of chemicals, water, energy, etc. (Tables 2, 3).

Table2. *Cost of initial biomass, chemicals, water and electric energy*

Item	Cost
Initial pulp	\$350 per ton
95% H_2SO_4	\$75 per ton
Hydroxylapatite	\$100 per ton
Na_2CO_3	\$150 per ton
Water	\$8 per 10 m^3
Electric energy	\$50 per MWh

Table3. *Expenses for production of 40% wetcake of NCP*

Item	Amount	Expense, \$
Initial pulp	1 ton	350
60% H_2SO_4	5 ton	240
Hydroxylapatite	4.4 ton	440
Na_2CO_3	0.1 ton	15
*Water	10 m^3	0
Electric energy	5 MWh	250
Subtotal 1:		1,295
**Overheads	15%	195
Subtotal 2:		1,489
By-product	7.23 ton	-1,085
Total:		**404**

**Since water is returned to production line, its expense is close to zero;*

***Overheads include salary, amortization, tax, etc.*

If sell 7.23 ton of the valuable by-product (superphosphate fertilizer) for \$150 per ton, the income will be \$1085, which can cover more than 70% of the production cost of nano-product, i.e. 40% wetcake of NCP. Considering that the final yield of NCP from 1 ton of initial pulp is 620 kg (0.62 t dry or 1.55 t wet product), the final production cost (PC) of cellulose nano-product, will be: PC = \$404/1.55 ton = \$260 per ton of wetcake.

CONCLUSION

The green and cost-save technology for production of nanocrystalline cellulose particles (NCP) was proposed. The parameters of acid hydrolysis of bleached Kraft pulp (SA) were studied. As a result the following optimal conditions were found: concentration of SA is 60 wt. %, LSR is 5, temperature is 45°C and time is 1h. Cellulose hydrolysis under optimal conditions generates NCP with average sizes of 120 x 15 nm, yield of 60-64 %, crystallinity degree of 73-75%%, DP of 120-140 and content of sulfonic groups of 46-50 meq/kg. The proposed technology provides the complete utilization of acidic wastewater and their use for the production of valuable by-product, superphosphate fertilizer, the selling of which covers above 70% of the production cost of NCP. Furthermore, washing water is returned in the production line. Thus, the cellulose nano-product, such as 40% wetcake of NCP, can be obtained with increased yield for relative low cost estimated at \$260 per ton of wetcake without discharge of production waste into the environment.

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Michael Ioelovich, has completed his PhD at the age of 27 years. Now he is scientific consultant of Polymate-INRC Ltd, Israel. His scientific activity is connected with chemistry, technology and nanotechnology of biomass, cellulose and synthetic polymers, as well as with chemistry and technology of biochemicals and biofuels. Dr. Michael Ioelovich is author of 13 monographs and book chapters, over 300 articles and 14 patents, which have been cited over 1000 times. Dr. Michael Ioelovich serves also as reviewer and editorial board member of some reputed journals.